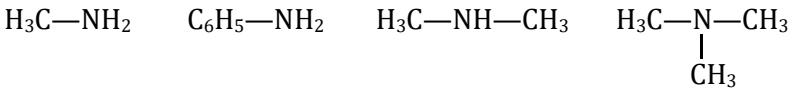
TG: @Chalnaayaaar

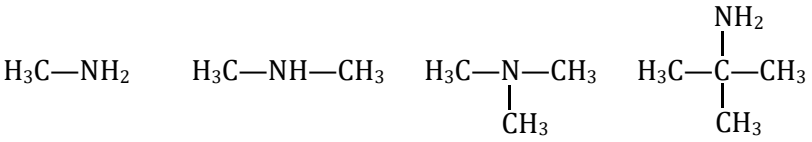
05 Amines

Amines can be considered as derivatives of ammonia obtained by replacement of one, two or all the three hydrogen atoms by alkyl/aryl groups.



Classification of Amines

Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom.

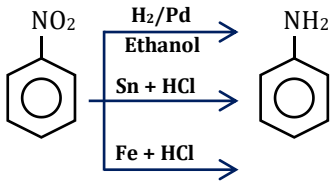


Primary (1°) Secondary (2°) Tertiary (3°) Primary (1°)

Methods of Preparation of Amines

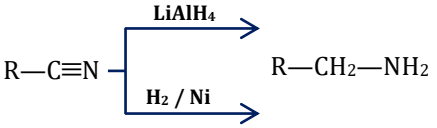
1. Reduction of nitro compounds :

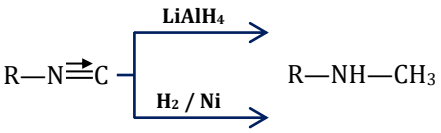
Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium.



2. Reduction of nitriles(cyanides) and isonitriles (isocyanides) :

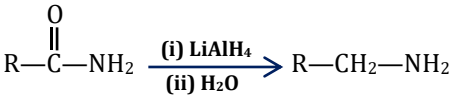
Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines but isonitriles produce secondary amines.





3. Reduction of amides :

Amides on reduction with lithium aluminium hydride ($LiAlH_4$) produce amines.



TG: @Chalnaayaaar

4. Ammonolysis of alkyl halides :

Alkyl halide on reaction with ethanolic solution of ammonia undergoes nucleophilic substitution in which the halogen atom is replaced by amino ($-NH_2$) group. The process of cleavage of C-X bond by ammonia is known as Ammonolysis.

$$NH_3 + R{-}X \longrightarrow R{-}NH_2$$

$$R{-}NH_2 + R{-}X \longrightarrow R{-}\underset{\displaystyle R}{\underset{|}{N}}H$$

$$R{-}\underset{\displaystyle R}{\underset{|}{N}}H + R{-}X \longrightarrow R{-}\underset{\displaystyle R}{\underset{|}{N}}{-}R$$

$$R{-}\underset{\displaystyle R}{\underset{|}{N}}{-}R + R{-}X \longrightarrow R{-}\overset{\displaystyle R}{\overset{|}{\overset{\oplus}{N}}}{-}R\,\overset{\ominus}{X}$$

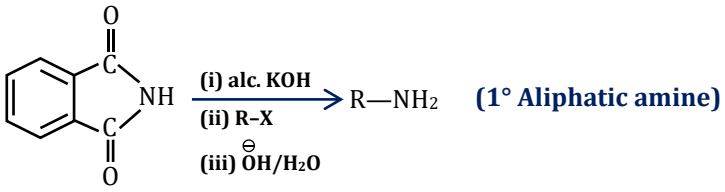
Quaternary ammonium salt

Ammonolysis reaction yields a mixture of primary, secondary, tertiary amines and also quaternary ammonium salt. However primary amine can be obtained as major product taking large excess of ammonia and quaternary ammonium salt will be major product if alkyl halide is taken in excess.

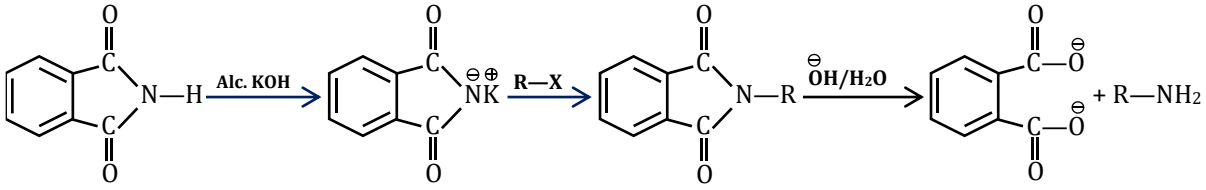
5. Gabriel phthalimide synthesis :

Gabriel synthesis is used for the preparation of 1° aliphatic amines.

Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on reaction with alkyl halide followed by alkaline or acidic hydrolysis produces the corresponding primary amine.



Mechanism



Phthalimide | Potassium salt of phthalimide | N-Alkylphthalimide | (1° amine)

6. Hoffmann bromamide degradation reaction :

$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2 + Br_2 + 4NaOH \longrightarrow \underset{\text{(1° amine)}}{R{-}NH_2} + Na_2CO_3 + 2H_2O + 2NaBr$$

Reagents that may be used for this reaction

1. X_2 + alkaline medium
   Br_2 + NaOH
   Br_2 + KOH
2. NaOX (NaOCl, NaOBr etc.)
   KOX (KOCl, KOBr etc.)

TG: @Chalnaayaaar

TG: @Chalnaayaaar

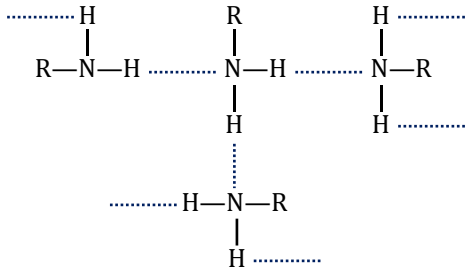
Physical Properties of Amines

Solubility

1. Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules.
2. Solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part.
3. Higher amines are essentially insoluble in water.

Boiling point

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule.



This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it.

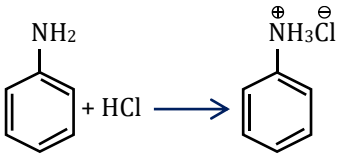
Tertiary amines do not have intermolecular association due to the absence of hydrogen atom required for hydrogen bond formation.

The order of boiling points of isomeric amines is as follows:
Primary > Secondary > Tertiary

Chemical Reactions of Amines

(1) Reaction showing basic nature :

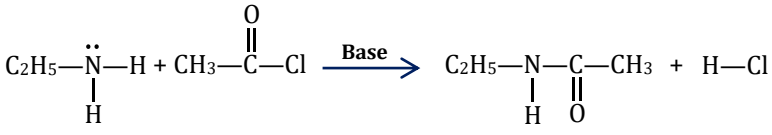
Amines being basic in nature react with acids to form salts.



Amine salts on treatment with a base like NaOH, regenerate the parent amine.

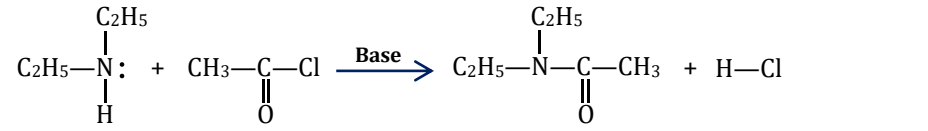
(2) Acylation reaction :

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction.

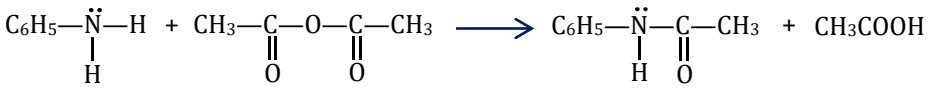


Ethanamine — N-Ethylethanamide

TG: @Chalnaayaaar



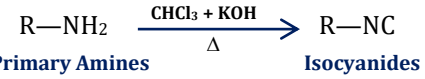
N-Ethylethanamine — N,N-Diethylethanamide



Aniline/ Benzenamine — Acetic anhydride — N-Phenylethanamide or Acetanilide

(3) Hoffmann's carbylamine reaction or isocyanide test :

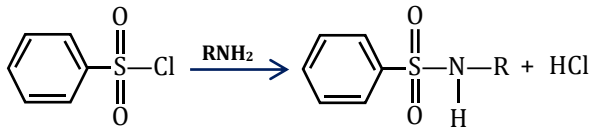
Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.



Primary Amines (aliphatic or aromatic) — Isocyanides

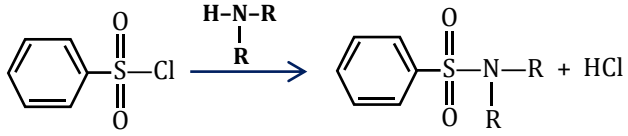
Note: Dichlorocarbene is formed in this reaction.

(4) Reaction with Benzenesulphonyl chloride (Hinsberg's reagent) :



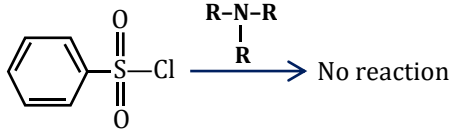
(N-alkylbenzenesulphonamide)

(soluble in alkali)

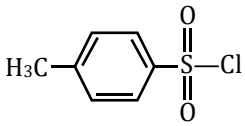


(N,N-dialkylbenzenesulphonamide)

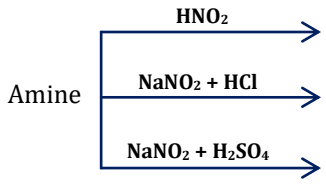
(insoluble in alkali)



Note: Hinsberg test is used to distinguish between primary, secondary and tertiary amines. These days benzenesulphonyl choride is replaced by p-toluenesulphonyl chloride (TsCl)



(5) Reaction with nitrous acid (HNO_2) :



TG: @Chalnaayaaar

TG: @Chalnaayaaar

(a) 1° Aliphatic amine

$$R—NH_2 \xrightarrow{NaNO_2+HCl} ROH + N_2 + HCl$$

Mechanism

$$NaNO_2 + HCl \rightleftharpoons HNO_2 + NaCl$$

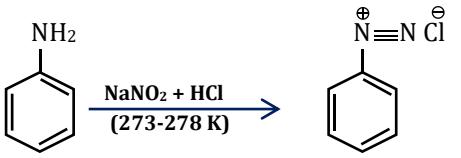
$$O=N—OH \overset{\oplus H}{\rightleftharpoons} O=N—\overset{\oplus}{O}\begin{matrix}H\\H\end{matrix} \rightleftharpoons \overset{\oplus}{N}=O + H_2O$$

nitrosonium ion

$$R—NH_2 + O=\overset{\oplus}{N} \longrightarrow R—N=\overset{\oplus}{N} \longleftrightarrow R—\overset{\oplus}{N}\equiv N \longrightarrow \overset{\oplus}{R} + N_2 \xrightarrow{H_2O} ROH$$

(Diazonium ion) (highly unstable) — (major)

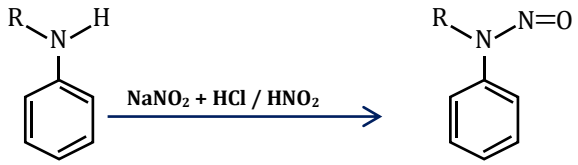
(b) 1° Aromatic amine



(Benzene diazonium chloride)

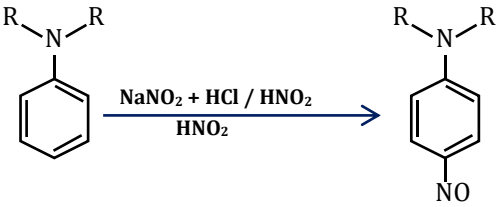
If the temperature of the diazonium salt solution is allowed to rise upto 283K, the salt gets hydrolysed to phenol.

(c) 2° Aromatic amine



N-alkyl-N-nitrosoaniline
(yellow oily liquid)

(d) 3° Aromatic amine

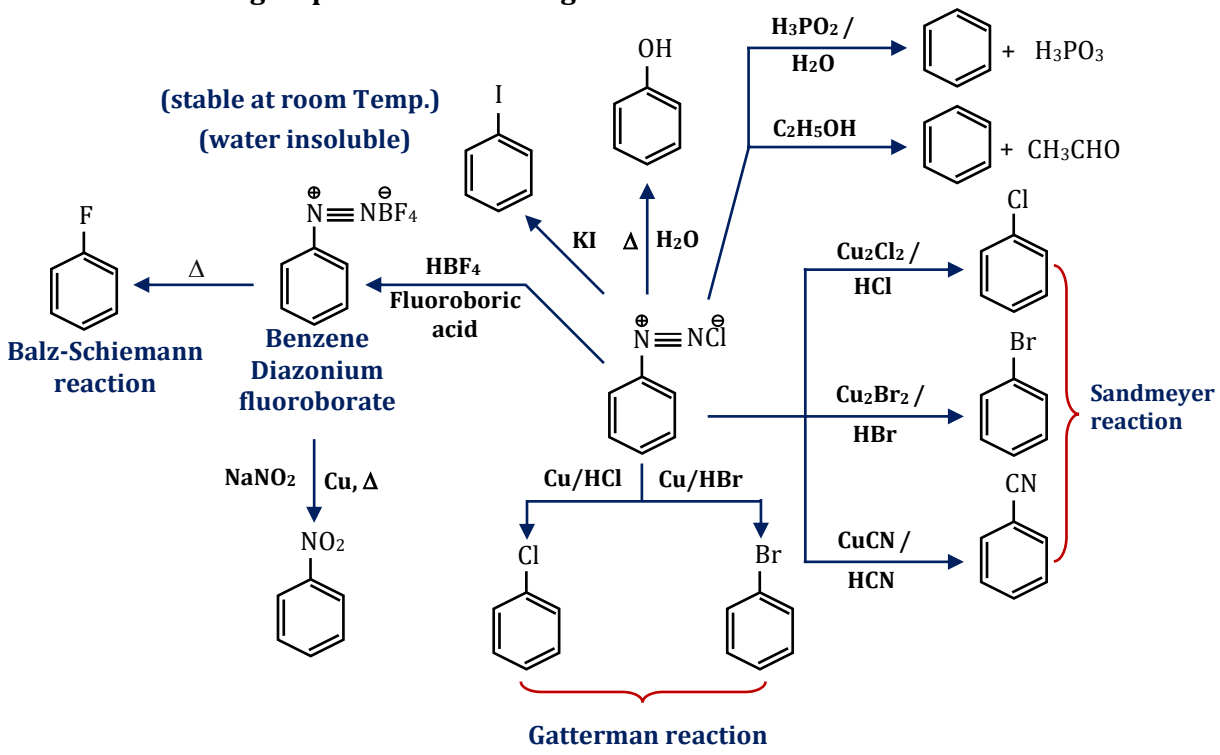


p-Nitroso-N,N-dialkylaniline

TG: @Chalnaayaaar

Chemical reaction of Diazonium salts

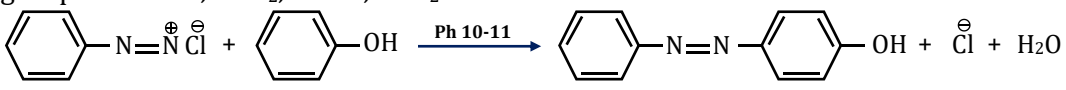
A. Reactions involving displacement of nitrogen :



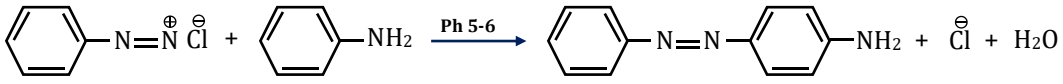
B. Reactions involving retention of diazo group :

Coupling reaction of benzene diazonium chloride (ESR)

Benzene diazonium chloride reacts with aromatic compounds containing strongly activating groups like –OH, $–NH_2$, –NHR, $–NR_2$



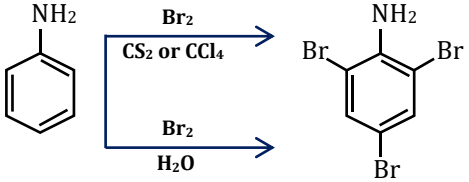
p-Hydroxyazobenzene
(orange dye)



p-Aminoazobenzene
(yellow dye)

(6) Electrophilic Substitution Reaction (ESR) :

Halogenation of Aniline



2,4,6–Tribromoaniline
(white ppt.)

TG: @Chalnaayaaar

Nitration of Aniline

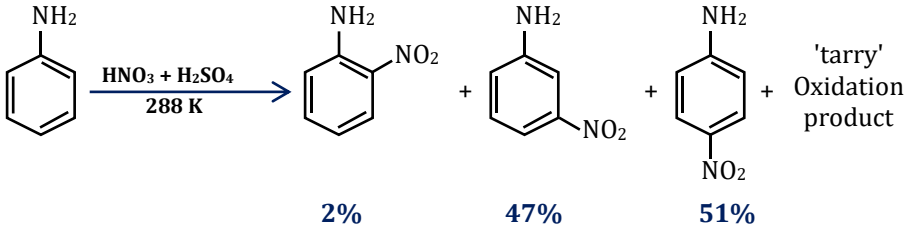
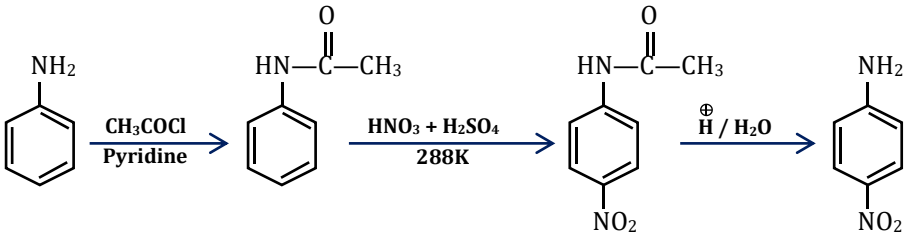
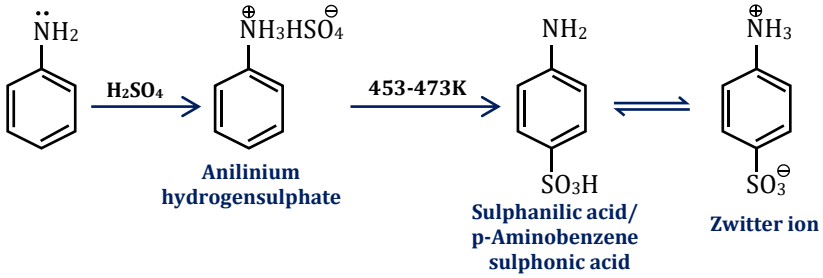


Illustration 1:



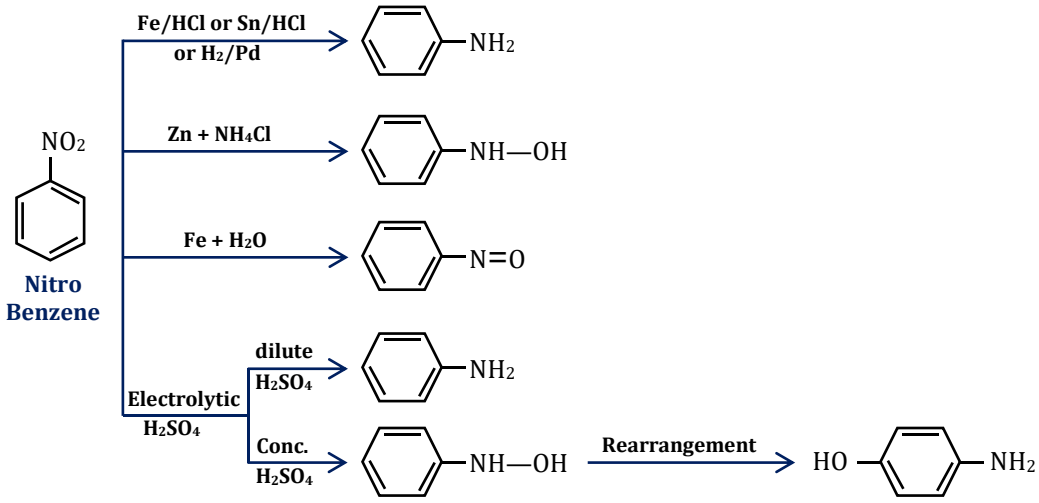
Sulphonation of Aniline



Note:

Aniline does not show Friedel Crafts reaction (alkylation and acylation)

Reduction of Nitrobenzene



TG: @Chalnaayaaar